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**REACTIVE MONOMERS AND THE
ADHESIVES AND POLYMERS THEREOF**

1 This invention relates to reactive monomers containing 2-cyanopenta-2,4-dienoate and methacrylic or acrylic double bonds in their molecules and the adhesives and polymers thereof.

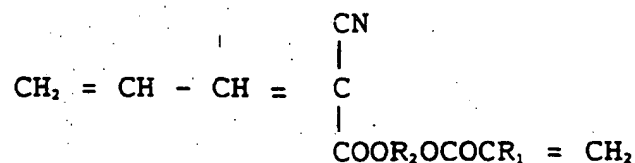
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Esters of the 2-cyanopenta-2,4-dienoic acid have been reported in the patent literature. The ethyl (US 3,316,227), alkenyl and alkoxyalkyl (US 3,554,990) esters have been particularly described. These monomers can polymerize under the influence of weak alkali and are suitable for adhesives. Their use as modifiers to cyanoacrylate adhesives (US 4,425,471) and for the manufacture of photoresists (EP 0404 446 A2) has also been reported.

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The present invention provides reactive monomers containing 2-cyanopenta-2,4-dienoic and methacrylic or acrylic double bonds, the polymers and adhesives thereof. The monomers of the present invention have the formula:

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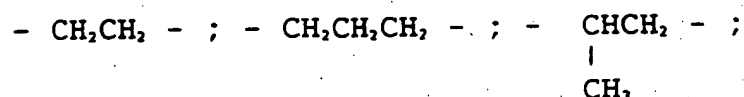
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where R_1 is H or CH_3 , R_2 is alkyl, alkenyl, alkynyl, alkoxyalkyl, poly(oxyalkyl), aryl, cycloalkyl or an aromatic heterocyclic radical. R_2 may also be one of the foregoing moieties substituted with one or more other of the moieties; this includes the case of a substituent itself being substituted. Group R_2 may contain other compatible

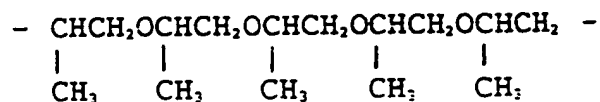
1 constituents, for example alkoxy, alkoxyalkoxy,
 carbalkoxyalkyl or halogen. In general, R_2 can be any
 moiety which does not contain a sufficiently nucleophilic
 group to initiate polymerization or sufficiently
 5 electrophilic group to interfere with polymerization. The
 alkyl or alkenyl moiety may be cyclic and normally R_2
 contains from 1 to 16 carbon atoms and often is a 1C, 2C,
 3C, 4C, 5C, 6C, 7C or 8C group, more usually it is a 1C-6C
 group. In the case of moieties containing a heterocycle,
 10 heteroatom ring members are normally counted as a carbon
 atom.

More preferably, R_2 is alkyl, alkoxyalkyl, poly(oxyalkyl),
 halogenated alkyl, alkenyl, alkynyl, phenyl, halogenated
 phenyl, phenylalkyl, alkoxyalkyl, alkoxyalkoxyalkyl,
 carbalkoxyalkyl or alkylideneglyceryl, wherein the terms
 "alkyl" and "alkenyl" include the corresponding cyclic
 radicals.

20 Specific examples of R_2 are



25 and



1 The reactive monomers of this invention are obtained by
reacting acrolein with



where R_1 and R_2 are the same radicals as described above.

5 The methacrylated or acrylated cyanoacetates are in turn
produced by reacting cyanoacetic acid with
hydroxylterminated methacrylate or acrylate monomer or by
transesterifying methyl or ethyl cyanoacetate with
hydroxylterminated methacrylate or acrylate monomer. A

10 preceding UK patent application by the same authors (UK Pat
Application No) describes the synthesis and
properties of these methacrylated and acrylated
cyanoacetates and could be followed to obtain the raw
materials. The reaction of acrolein with methacrylated or
15 acrylated cyanoacetates is chemically consistent in nature
to the reaction of acrolein with active methylene compound
as described in US 3,316,227. All of the considerations
derived in this reference hold true for the present
reaction between acrolein and methacrylated or acrylated
20 cyanoacetates.

A distinctive feature of the present reaction however, is
the reactivity of the active methylene compound which in
the present case contains polymerizable methacrylic or
25 acrylic bonds. Thus in order to avoid polymerization
during the reaction it is advisable to use phenolic-type
inhibitors, like hydroquinone and p-methoxyphenol, in
conjunction with air sparge of the reaction mixture.

1 If desired mixtures of two or more of the monomers of the invention with themselves or other monomers or polymers could be used.

5 Usually the reactive monomers of the present invention are stabilized with anionic and free-radical polymerization inhibitors. Anionic polymerization inhibitors could be soluble acidic gases (for example sulfur dioxide), hydrogen fluoride, phosphonic, carboxylic and organic sulfonic
10 acids, sultones, BF_3 and its complexes and phosphazenes, for example. The free-radical polymerization inhibitors are usually hydroquinone, p-methoxyphenol or t-butyl catechol, for example.

15 The inhibitors are normally used in small amounts of from 0.00001 to 1% by weight of the monomer. The preferred quantities for the above-mentioned inhibitors are: acidic gases - from 0.0001% to 0.06%; acids - from 0.0001% to 0.01%; sultones - from 0.01% to 0.1%; BF_3 - from 0.0001 to
20 0.01; phosphazenes - from 0.00001% to 0.001%; free-radical inhibitors - from 0.001% to 1%. The foregoing percentages are percentages by weight of the reactive monomer. It should be noted that the quantity of inhibitor will influence the onset of polymerization of the monomers of
25 the present invention and could be used as a means to control the set time.

1 The reactive monomers of the present invention may contain
polymerization initiators. They could be anionic
polymerization initiators like pyridine, aminopyridine,
vinylpyridine, methoxyethylpyridine, piperidine, picoline,
5 lutidine, N,N-dimethyl-p-toluidine, N,N-dimethyl-o-
toluidine, N,N-dimethyl-m-toluidine, triphenylphosphine,
triethylphosphine, tribenzylamine, triethylamine,
benzyl dimethylamine, diethylenetriamine,
benzyltriethylamine, tribenzylamine, poly (4-
10 vinylpyridine), calixarenes, tertiary amine-SO₂ complexes,
polyethyleneglycol, phenolformaldehyde resins,
vinylimidazole, triethanolaminatotitanium, aminosilanes,
phosphites, metal acetylacetonates, N-(oxydiethylene)
benzothiazole-2-sulfenamide, bismuth
15 dimethyldithiocarbonate, as well as alcohols, bases and
hydroxyl or amine group containing compounds.

They could also be cationic polymerization initiators.
Free-radical polymerization initiators such as
20 methylethylketone peroxide, cyclohexyl peroxide, cumene
hydroperoxide, dibenzoyl peroxide or redox systems for
generating free-radicals can be used. They are well known
in the art of polymerizing acrylate and methacrylate
monomers. Compounds which generate radicals or ions under
25 ultraviolet or electron-beam irradiation could also be used
to initiate polymerization of the reactive monomers of the
present invention. The various initiators could be used
alone or in conjunction with each other. In order to
impart desired properties to the monomers of the present

1 invention and to the properties of the resultant adhesive
bond or polymer as well as for economic considerations,
further additives can be introduced into them. They can
be, for example, any of the known polymeric thickeners and
5 viscosity regulators, rubbers, plasticizers and tougheners,
compatibilizers, thixotropic agents, colourants, deodorants
or perfumes, for example, used in cyanoacrylate adhesives
and in acrylic and methacrylic ester compositions and
polymers. The composition may also contain other monomers
10 containing a reactive double bond.

A distinctive feature of the reactive monomers of the
present invention is that they are easily polymerizable in
a variety of ways. Anionic initiation, most commonly
15 induced by the adsorbed on the objects' surface moisture
causes polymerization along the dienic double bonds,
yielding a polymer of substituted butadiene structure. The
pendant acrylic or methacrylic double bonds can be
additionally polymerized by heat, redox systems or UV or
20 EB irradiation to yield a cross-linked elastomeric
structure. In a different route of curing the acrylic or
methacrylic double bonds could be polymerized initially
yielding a polymethacrylate or polyacrylate with pending
cyanopentadienic double bonds. They in turn could be
25 polymerized by heat or moisture to produce similar to the
first instance cross-linked structure. The following
scheme illustrates the curing reaction that the monomers of
the present invention could undergo.

1 A distinctive feature of the reactive monomers of the
present invention is that as a result of polymerization
they can form strong adhesive bonds between a variety of
substrates, ie metals, plastics, rubbers, glass, wood,
5 paper, live soft or bone tissue. They can cure in a matter
of seconds to minutes. Depending on the type and degree of
cure the adhesive bond can vary from soft and rubbery to
tough and resilient. A distinctive characteristic of the
adhesive bond is that as a consequence of cross-linking it
10 is water and humidity resistant, heat resistant, impact and
peel resistant and can sustain large loads and stresses.

Application of the reactive monomers of the present
invention is in structural and industrial adhesives.

15 Another distinctive feature of the reactive monomers of the
present invention is that they spread easily over water or
biological fluids and then form a polymeric layer. This
property can be employed to utilize these monomers as
20 medical and surgical adhesives, particularly for bonding
bone tissue in which case the initial anionic
polymerization could be followed by radical cross-linking
to obtain cross-linked adhesive bond capable of sustaining
the loads at the fractured interface.

25 Another application of the reactive monomers of the present
invention is for coatings which can be produced by surface
moisture cure or by UV-light irradiation. They will be
particularly suitable for optical fibre coating.

1 Another application of the reactive monomers and polymers
thereof of the present invention is for manufacture of
positive or negative photo or electron beam resists. Their
controlled step-wise polymerization will produce ultra-high
5 resolution.

The above-mentioned applications are only indicative and do
not limit the scope of application of the reactive monomers
of the present invention, as well as the applications of
10 their adhesives and polymers.

The invention is illustrated by the following examples:

Example 1

15 21.9g of methacryloyloxyethyl cyanoacetate is mixed
together with 40ml of tetrahydrofuran. The mixture is
cooled to 4°C and 9g of zinc chloride is added during
mixing. The mixture is cooled again to 4° and 8.9ml of
acrolein are added dropwise over 5 minutes. The
20 temperature increases from 4°C to 8°C. The reaction flask
is removed from the ice water bath and left stirring for 8
hours at room temperature. To the clear yellow solution
obtained 50ml of toluene is added. The product is isolated
by three consecutive extractions with 100ml of 2N
25 hydrochloric acid. The organic layer is filtered through
filter paper. The filtrate is stripped from the solvent by
heating (90°C) under reduced pressure (0.7mmHg). A steady
stream of air through a capillary is maintained during the
stripping stage. 23.0g of methacryloyloxyethyl 2-

1 cyanopenta-2,4-dienoate are obtained. Its $n_D^{20} = 1,5139$. IR
spectrum (Figure 2) confirms the structure. A drop of the
product placed on water spreads and forms a polymeric film.
A drop of product placed between fingers, glass or metal
5 surfaces polymerizes instantly to give an adhesive bond.

Example 2

35.2g of methacryloyloxypropyl cyanoacetate is mixed with
50ml of dioxane. 13.5g of zinc chloride is added during
10 mixing. 13.25g of acrolein are added dropwise over 10
minutes, taking care the reaction temperature not to exceed
20°C. The stirring is continued for a further 8 hours at
room temperature yielding a clear yellow solution. 100ml
of methylmethacrylate are mixed in and then three
15 consecutive extractions with 150ml of 2N hydrochloric acid
are performed. The organic layer is filtered and stripped
under reduced pressure (0.7mm Hg). The pot temperature is
not to exceed 90°C and a steady stream of air through the
product is maintained during stripping. 25g of
20 methacryloyloxypropyl 2-cyanopenta-2,4-dienoate are
obtained with $n_D^{20} = 1,5045$. The IR spectrum (Figure 3)
confirms the chemical structure. The product possesses the
same adhesive properties as described in Example 1.

25

Example 3

20.4g of acryloyloxyethyl cyanoacetate containing 0.02g of
p-methoxyphenol are mixed together with 40ml of
tetrahydrofuran. Through a capillary a constant flow (4ml/
min) of dry air is sparged through the reaction mixture

1 during the reaction. The mixture is cooled to 4°C and 9.5g
of zinc chloride are added during mixing. The mixture is
cooled again to 4°C and 8.9ml of acrolein are added dropwise
over 5 minutes. The reaction temperature increases to 9°C.
5 The reaction flask is removed from the ice water bath and
left stirring for 8 hours at room temperature. To the
clear yellow solution obtained 50ml of toluene are added
and the product is isolated by three consecutive
extractions with 100ml of 2N hydrochloric acid solution.
10 The organic layer is filtered and stripped from solvents by
heating up to 90°C under reduced pressure of 0.7mm Hg. A
stream of air through a capillary is maintained during the
stripping stage. 13.3g of acryloyloxyethyl 2-cyanopenta-
2,4-dionate with $n_D^{20} = 1.5147$ are obtained. The IR
15 spectrum (Figure 4) confirms the chemical structure.

Example 4

23.17g of methacryloylhexa(oxyethyl) cyanoacetate
containing 0.035g of hydroquinone are mixed together with
20 33ml of dioxane. Through a capillary a constant flow
(4ml/min) of dry air is started and maintained during the
reaction process. 4.5g of zinc chloride are added during
stirring. The mixture is cooled to 20°C and 4.45ml of
acrolein are added dropwise over 5 minutes. The mixing is
25 continued at room temperature for 12 hours. To the clear
yellow solution 100 ml of methyl methacrylate are added.
The product is isolated by three consecutive extractions
with 100ml of 2N hydrochloric acid solution. The organic
layer is filtered and subjected to stripping by heating up

1 to 90°C under vacuum of 0.7mm Hg and the essential stream of
dry air. 18g of methacryloyl(oxyethyl) 2-cyanopenta-2,4-
dienoate, with $n_D^{20} = 1.4964$ are obtained. The IR spectrum
(Figure 5) confirms the chemical structure.

5

Example 5

Adhesive bonds based on the reactive monomers of the
present invention were prepared by placing a drop of
monomer on one metal surface to which the other was
10 manually pressed for 1 minute. Adhesive strength was
measured after 24 hours and after ageing for 24 hours at
various temperatures. The specimen had dimensions in
accordance with ASTM D1002 for the sheer strength and ASTM
D897 for the tensile strength determinations. The steel
15 surfaces were roughened with extra fine sandpaper and
degreased with methylene chloride. No chemical treatment
of the surfaces was employed. The testing procedure
followed the above mentioned standards. Each reported
value is average of 10 determinations. The obtained
20 results are summarized in Table 1.

Table 1

Adhesive strength of steel/steel joints bonded with methacrylated and acrylated 2-cyanopenta-2,4-dienoates

No	2-cyanopenta-2,4-dienoate	Mode of testing	Adhesive strength (kg/cm ²) after 24 h at				
			20°C	100°C	125°C	150°C	200°C
1	methacryloyloxyethyl	tensile	70	172	184	77	62
		shear	56	123	132	61	61
2	methacryloyloxypropyl	tensile	54	77	100	46	18
		shear	39	112	69	66	48
3	acryloyloxyethyl	tensile	52	121	232	161	178
		shear	35	120	112	108	76
4	acryloyloxypropyl	tensile	36	78	130	158	148
		shear	20	135	117	149	107
5	methacryloylhexa(oxyethyl)	tensile	19	27	28	28	43
		shear	10	12	37	38	38
6	methacryloylpenta(oxypropyl)	tensile	6	10	14	16	60
		shear	7	10	14	19	65

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Example 6

Adhesive bonds between glass/glass and glass/steel were prepared in the same fashion as described in Example 5.

5

The glass surface was only degreased with methylene chloride. The glass/glass joints and the glass portion of the glass/steel joints were in turn bonded in larger areas to steel coupons so that they rather than the fragile glass could be gripped in the testing machine. The obtained results are presented in Table 2.

Table 2

Glass joints bonded with methacrylated and acrylated cyanopentadienoates

No	2-cyanopenta-2,4-dienoates	Substrates	Mode of testing	Adhesive strength (kg/cm ²) after 24 h at				
				20°C	100°C	150°C	200°C	250°C
1	methacryloyloxyethyl	glass/glass	tensile	69	NT	NT	NT	NT
		glass/steel	tensile	150	NT	NT	NT	NT
2	methacryloyloxypropyl	glass/glass	tensile	35	NT	NT	NT	NT
		glass/steel	tensile	134	NT	NT	NT	NT
3	acryloyloxyethyl	glass/glass	shear	>20*	>20*	>20*	>15*	NT
		glass/steel	tensile	47	35	13	6	NT
4	methacryloylhexa(oxyethyl)	glass/glass	tensile	5	22	21	20	NT
		glass/glass	shear	>20*	>20*	>20*	>20*	NT
		glass/steel	tensile	11	12	13	NT	NT
5	methacryloylpenta(oxypropyl)	glass/glass	tensile	4	4	4	13	22
		glass/steel	shear	3	3	8	>20*	>20*
		glass/steel	tensile	5	5	27	38	35

NT- not tested
 * - glass substrate failure

1

Example 7

Various substrates were bonded with acryloyloxyethyl 2-cyanopenta-2,4-dienoate following the described procedure.

The obtained results are presented in Table 3.

5

Table 3

**Adhesive strength of various substrates bonded with
acryloyloxyethyl 2-cyanopenta-2,4-dienoate**

No	Substrates	Mode of testing	Adhesive strength (kg/cm ²) after 24 h at				
			20°C	55°C	80°C	100°C	150°C
1	balsa wood/balsa wood	shear	12 (c)	>20 (s)			
2	paper/paper	shear	>3.5 (s)				
3	carton/carton	shear	>5 (s)				
4	teflon/teflon	shear	3 (c)			7 (a)	7 (a)
5	polypropylene/polypropylene	shear	3 (c)	12 (a)	15 (a)		
6	polycarbonate/polycarbonate	shear	14 (c)			20 (a)	41 (c)
7	UPVC/UPVC	shear	11 (c)		14 (a)		
8	polyacrylate/polyacrylate	shear	6 (c)	25 (a)			
9	steel/polyacrylate	shear	24 (c)		35 (a)		
		tensile	48 (c)		56 (a)		
10	steel/UPVC	shear	8 (a)		37 (a)		
		tensile	16 (a)		34 (a)		
11	steel/polycarbonate	shear	21 (a)			32 (c)	
		tensile	30 (a)			15 (a)	15 (a)
12	steel/teflon	shear	5 (a)			6 (a)	6 (a)
13	steel/polypropylene	shear	15 (a)	21 (a)		31 (a)	
14	steel/polyethylene	shear	4 (c)	37 (a)			
		tensile	5 (c)	27 (a)			

(s) - substrate fails

(c) - cohesive type of bond failure

(a) - adhesive type of bond failure

1 **Example 8**

UV light curable compositions were prepared by dissolving into the reactive monomers of the present invention 1% by weight of 1-hydroxy-cyclohexyl-phenyl-ketone. A drop of
5 the composition was spread between glass/glass or glass/steel surfaces and subjected to UV radiation (with intensity of 7mW/cm^2 at 365nm and 4mW/cm^2 at 310 nm) for 2 minutes. The strength of the obtained adhesive bonds were measured following the irradiation and also following
10 additional thermal treatment for 24 hours. The obtained results are presented in Table 4.

Table 4.

Glass joints bonded by UV-cured cyanopentadienoate monomers

No	2-cyanopenta-2,4-dienoate	Substrates	Testing mode	Adhesive bond strength (kg/cm ²)			
				20 °C	100 °C	150 °C	200 °C
1	acryloyl-oxyethyl	glass/glass	shear	> 20 (s)	> 20 (s)	> 20 (s)	> 20 (s)
			tensile	11 (a)	> 42 (s)	> 41 (s)	> 40 (s)
		glass/steel	shear	14 (a)	> 18 (s)	> 17 (s)	> 17 (s)
			tensile	25 (a)	63 (a)	38 (a)	36 (a)
2	methacryloyl-penta(oxypropyl)	glass/steel	tensile	7 (c)	13 (a)	39 (a)	38 (a)

(s) - substrate fails

(a) - adhesive type of bond failure

(c) - cohesive type of bond failure